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(54) Title: TIME-OF-FLIGHT MASS SPECTROMETER

(57) Abstract

A mass spectrometer of the time-of-flight kind includes an ion source which produces ions for analysis which on emergence from the source have a velocity in a first direction. The ions pass between a pair of electrodes to one of which a voltage is provided which imposes a velocity in a second direction onto the ions to carry them into a measurement chamber containing a detector. Ions of interest of a particular m/z ratio are selected, fragmented in a fragmentation device and detected by the detector which produces a mass spectra in accordance with the detected smaller mass ions. The ions of interest are selected by passing the ions through a pair of electrodes, one of which has a voltage applied to it which creates an electric field which reduces only the ions of interest to substantially zero velocity in the second direction in the vicinity of the fragmentation device. The velocity in the first direction then causes only the ions of interest into the fragmentation device for fragmentation.

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TIME-OF-FLIGHT MASS SPECTROMETER

This invention relates to improvements in or relating to mass spectrometers of the time-of-flight kind.

5   For some measurements it can be advantageous to use a tandem time-of-flight mass spectrometer. A tandem mass spectrometer usually comprises two linked mass spectrometers, the first mass spectrometer being used to separate ions of interest from inorganic, bio-organic or organic compounds and then the ion of interest is fed into a fragmentation device

10   where this ion is fragmented into smaller ions which produce a mass spectrum which is characteristic of the structure of the ion of interest and is detected using a second mass spectrometer.

It will be appreciated that whilst use of a tandem mass spectrometer in the manner mentioned above increases the amount of information which

15   can be determined about an ion of interest, the cost and complexity of apparatus necessary to perform such measurements can be excessive, especially bearing in mind that two separate or linked mass spectrometers are required.

It is an object of the present invention to provide a mass

20   spectrometer of the time-of-flight kind which can provide an equivalent amount of information about an ion of interest to that which can be provided by a conventional tandem mass spectrometer.

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It is further an object of the present invention to provide a mass spectrometer which is relatively simple in construction and therefore relatively low in cost compared to other tandem time-of-flight mass spectrometers.

5   It is still further an object of the present invention to provide a mass spectrometer which can operate both as a single spectrometer and also as a tandem spectrometer.

According to the present invention therefore there is provided a mass spectrometer of the time-of-flight kind comprising an ion source to produce ions for analysis, said ions having a velocity in a first direction, means to impose a velocity in a second direction on said ions to cause the ions to enter a measurement chamber in which is disposed a detector, means to reduce the velocity of ions of interest of a selected m/z ratio in said second direction to substantially zero whereby the velocity in a first direction causes only said ions of interest to enter a fragmentation means which acts to fragment the ions into smaller mass ions, means to impose a further velocity in a second direction on said smaller mass ions to cause said smaller ions to move towards the detector for detection, said detector being operable to produce a mass spectrum in accordance with said detected smaller mass ions.

With this arrangement it is possible to provide a time-of-flight mass spectrometer which can, if desired, provide the same amount of measured

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information as a conventional tandem spectrometer but in which it is only

necessary to use a single measurement chamber, thereby reducing cost and

complexity. Furthermore, measurements can be made in the same manner

as a single time-of-flight spectrometer or a tandem spectrometer.

5   The invention will now be described further by way of example only

and with reference to the accompanying drawings of which:-

Fig. 1 shows a diagrammatic representation of

one form of time-of-flight mass spectrometer in

accordance with the present invention;

10   Fig. 2 shows the spectrometer of Fig. 1 with the

path of travel of fragmented ions shown; and

Fig. 3 shows a diagrammatic sectional side view

of one form of fragmentation device for use in the

mass spectrometer of Fig. 1; and

15   Fig. 4 shows a schematic perspective view of an

alternative form of time-of-flight spectrometer in

accordance with the present invention.

Referring now to Fig. 1, there is shown a mass spectrometer of time-

of-flight form in accordance with the present invention.

20   The spectrometer comprises an ion source 10 which produces a beam

of ions, an ion optical arrangement 20 which acts to focus and accelerate

the ion beam produced by the ion source, an extraction device 30 which

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acts to orthogonally extract from the beam of ions produced by the ion source 10, a small part thereof which is to be fed into the measurement chamber 50 of the mass spectrometer for analysis, an ion mirror 40, a fragmentation device 60 which acts to fragment selected ions of interest

5   into a number of smaller mass ions and a detector device 70 to detect incident ions and from the output of which a mass spectrum can be produced which is characteristic of the incident ions.   All of the abovementioned components are contained within a vacuum envelope.

The ion source 10 is of conventional form and may form ions utilising

10   any suitable means of ionization as desired or as appropriate. For example, the ion source may use electron impact, chemical ionization, thermo or electro spray ionization, fast atom bombardment or any other suitable means of ionization. The ion source can generate either a continuous beam or a pulsed beam of ions, as desired or as appropriate.

15   The ion optical arrangement 20 contains any suitable arrangement which can act to focus the beam produced by the ion source to a narrow low-divergence beam.

The extraction device 30 comprises electrodes 31 and 32 which extend generally in the direction of travel of the beam of ions produced by

20   the ion source. In the embodiment shown in Fig. 1, the electrodes 31 and 32 are generally similar in shape, but of course it will be appreciated that the electrodes can be of any suitable shape. At least electrode 32 which

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is positioned adjacent to the measurement chamber 50 is either in the form

of a perforated grid or has a slot or aperture (not shown) therein through

which ions can pass for a reason to be described hereinafter.

The measurement chamber 50 is generally of conventional form and

5   is provided with a perforated grid electrode 34, or an electrode having slits

therein through which ions can pass, in a wall substantially adjacent and

parallel to the perforated grid electrode 32, or slit electrode, of the

extraction device 30 whereby ions can pass from the extraction device 30

into the measurement chamber 50, or vice versa, via the perforations or slit

10   in the electrodes 32 and 34. A detector 70 of conventional form is located

within the measurement chamber 50. The position of the detector within

the measurement chamber is of importance for a reason which will become

apparent hereinafter. At an opposite end of the measurement chamber 50

to the perforated grid or slit electrode 34, there is provided an ion mirror 40

15   of conventional form.

The fragmentation device 60 acts to fragment selected ions of

interest into ions of smaller masses. The fragmentation device 60 is located

adjacent an end 35 of the extraction device 30 opposite to the ion source

10. The fragmentation device 60 can operate to fragment the ions in any

20   of a number of conventional ways, for example by collision with gas

molecules at high pressure (collision induced dissociation - CID), by

smashing the ions against a fixed surface (surface induced dissociation -

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SID) or by fragmentation of the ions within a light beam (photo induced dissociation - PID).

One form of fragmentation device 60 is shown more clearly in Fig. 3. This fragmentation device comprises a fragmentation region defined

5   between the conducting restrictors 61 which are shaped so as to define an inlet aperture at one end. An opposite end of the fragmentation region is defined by an end cap 62 which may have a transparent or at least translucent window 63 there for a purpose which will become apparent hereinafter. A gas leak valve 64 may also be provided linked to the

10   fragmentation device, along with an ionization gauge 65. A radio frequency ion guide 66 extends generally along a horizontal axis of the device for a reason which will also become hereinafter apparent. Any form of ion optics, static or dynamic may be used within the fragmentation device 60.

In use, an ion beam is produced by an ion source 10 which exits the

15   source in a direction generally parallel to the direction indicated Y in Figure 1. The ion beam passes through the ion optical arrangement 20 in which the beam is focused into an ion beam of low divergence. The narrow low-divergent beam of ions are directed so as to pass between electrodes 31 and 32 which form a part of the extraction device 30. As the ion beam

20   enters the region between the electrodes 31 and 32, a pulse of voltage is applied to the electrode 31 using a pulsed voltage supply 33. The electrode 32 is maintained at a fixed potential whilst electrode 31 is pulsed to a

voltage V greater than the fixed potential at which electrode 32 is maintained. Alternatively, electrode 32 can be pulsed to a voltage lower than a fixed voltage at which electrode 31 is maintained. The difference in voltage V between electrode 31 and electrode 32 causes an electric field

5   orthogonal to the direction Y and generally in the direction X indicated on Fig. 1. If electrode 31 is pulsed to voltage V, it will be understood that a section of the beam of ions travelling along the extraction device 30 between electrodes 31 and 32 will experience an electric field E which will cause them to accelerate transversely of electrode 31 towards electrode 32.

10   Electrode 32 is arranged to be formed either from a perforated grid or to have a slit therein in order that ions can pass through this electrode under the influence of the field E and into the measurement chamber 50 of the spectrometer through a similar electrode 34 provided in the wall of the chamber adjacent electrode 32. If desired, the beam can be further

15   accelerated between electrodes 32 and 34. If desired further electrodes may be provided for this purpose. If the voltage is applied rapidly, it can be seen that a rapid and efficient acceleration of a segment of ion beam into the measurement chamber 50 of the spectrometer can be achieved.

When the section of the ion beam enters the measurement chamber

20   50 of the mass spectrometer after its orthogonal extraction in the device 30, the ions within the section of the beam will not only have a velocity in the direction X, due to acceleration between electrodes 31, 32 and 34, but

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will also substantially retain their component of velocity in the direction Y

and therefore the path followed by the ion beam section will be that shown

in the diagram of Fig. 1 marked P_1. Hereafter any component of velocity in

the direction Y will be referred to as Y-velocity and correspondingly any

5   component of velocity in the direction X will be referred to as X-velocity.

Since ions within the ion beam produced by the ion source 10 which are

closer to electrode 31 prior to application of the voltage V to this electrode

31, will inevitably acquire a greater amount of energy as they move a

greater distance through the electric field $\underline{E}$, such ions will inevitably have

10   a greater X-velocity when they enter the chamber 50 of the mass

spectrometer than ions which were initially in a part of the ion beam closer

to electrode 32. Due to their greater X-velocity, there will be a plane,

shown as a dotted line Q in Fig. 1, within the measurement chamber 50 in

which these ions will have caught up with those ions which started from a

15   position closer to electrode 32 and this plane Q. The detector may be

situated at this plane Q. As the ions move beyond plane Q within the

measurement chamber 50 along their path of travel, the ions with a higher

X-velocity will move ahead of the ions with a lower X-velocity. In order to

compensate for this, at one end of the measurement chamber 50 opposite

20   to the point of entry of the ions into the measurement chamber, an ion

mirror 40 is provided. The ions, as they move through the measurement

chamber 50, will interact with the ion mirror 40. The ion mirror acts to

reflect ions which interact with it so as to cause them to travel in the opposite X-direction. However, the interaction with the ion mirror 40 varies according to the X-velocity of the ions as they enter the ion mirror. The greater the X-velocity of ions, the greater the depth with which these ions

5   penetrate the ion mirror 40 and accordingly it will be realised that it can be arranged by suitable choice of ion mirror 40 for the higher X-velocity ions to penetrate sufficiently far into the ion mirror 40 compared to lower X-velocity ions whereby after reflection the lower X-velocity ions emerge from the ion mirror 40 travelling in the opposite X-direction ahead of the higher

10   X-velocity ions. An ion mirror 40 of this type is usually referred to as a "reflectron".

After reflection at the ion mirror 40 it can be arranged that the section of ion beam is directed so as to impinge upon the detector 70 whereby the masses of the ions can be detected in conventional single time-

15   of-flight mass spectrometer manner. In this case it may be arranged such that, after reflection, the higher X-velocity ions catch up with the lower X-velocity ions, at the detector 70.

However, the present invention is primarily concerned with operation of the mass spectrometer in a tandem manner.

20   By arranging for the voltage applied to the electrode 31 to be at a selected predetermined value, it can be arranged that after reflection within the ion mirror 40 the beam section is directed so as to pass the detector 70

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along a second path P_2 shown in Fig. 1 and to exit the measurement

chamber 50 via electrode 34 and electrode 32. Ions will then be

decelerated by the voltage difference between electrodes 31 and 32 and 32

and 34 in the opposite manner to which they are accelerated on entry to the

5   chamber 50. At some point in time, ions of interest of a given mass/charge

ratio will be decelerated to substantially zero X-velocity and after this point

in time will be turned around and accelerated in the opposite direction. It

can be seen in Fig. 1 that the arrangement of the present invention is

substantially symmetrical with respect to forces in the X-direction and, if the

10   voltage V on electrode 31 is switched off at the time the ion of interest

(with the given mass/charge ratio) has substantially zero X-velocity, the ion

of interest will continue to move along the direction Y due to the Y-velocity

imposed from extraction from the ion source. Thus the ion of interest will

enter the fragmentation device through the aperture 61. The ions of

15   interest which enter the fragmentation device 60 will appear to all intents

and purposes as if they had simply travelled directly from the ion source 10

between electrodes 31 and 32 to the fragmentation device 60. At this point

in time at which the ion of interest is at substantially zero X-velocity, ions

of other mass/charge values which are not of interest will not have

20   substantially zero X-velocity and will therefore have an X-Velocity which will

carry them towards electrode 31 or, if they have already been turned round

by electrode 31, towards electrode 32. Ions of mass/charge value close to

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the ion of interest will also retain an X-velocity when the voltage to

electrode 31 is switched off and these will therefore run at an angle to the

direction Y and therefore if the aperture to the fragmentation device 60 is

arranged to be of a permitted size, ions of mass/charge value, other than

5   that of the ion of interest can be prevented from entering the fragmentation

device 60.   Therefore, in this way, an ion of interest with a particular

mass/charge ratio can be selected for fragmentation.   Within the

fragmentation device the ion of interest is fragmented into ions of smaller

mass utilising one of the fragmentation methods mentioned above and, to

10   achieve highest transmission of ions and maximum mass resolution, angular

acceptance (α) of the fragmentation device 60 should be

$$\alpha \approx \frac{\delta v_x}{v_y} \approx \frac{V}{V_0} \cdot \frac{L_{\mathit{eff}}}{4 \cdot R \cdot d} \cdot \sqrt{\frac{V_0}{E}}$$

15   where E is the mean initial acceleration voltage in the ion source 10 and ion

optical arrangement, δv_x is the spread of velocities in direction X resulting

from aberrations in the mass spectrometer, v_y is the mean velocity in the

direction Y, R is the mass resolution as a single mass spectrometer

(measured on the same level of ion distribution as δv_x). V is a voltage

20   applied across the gap d between electrodes 31 and 32, L_{eff} is effective path

length of ions between pulses (i.e. the mass-independent multiplication of

mean velocity in the direction X and time-of-flight between moments of

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push-out and turning in the extraction device 30), V_e is the mean voltage difference passed by ions during the transverse acceleration. Once the fragmented ions have been formed, they are ejected in a manner to be described from the fragmentation device into the extraction device 30 and

5   a pulsed voltage applied to electrode 31 will once again cause the fragmented ions to move generally transversely in the direction X back into the measurement chamber 50 via electrode 32 and electrode 34. The ions of interest as mentioned above enter the fragmentation device 60 via aperture in the conductivity restrictor 61. Within the fragmentation device

10   60, the ions of interest are fragmented into smaller ions using either multiple low energy collisions with gas molecules (CID), or can be directed towards the end cap 62 against which they smash and are fragmented (SID). Alternatively an intense light beam can be directed at the ions of interest through window 63 in order that the ions can be fragmented (PID). When

15   collision with gas molecules is being used for fragmentations, gas is introduced into the fragmentation region through a leak valve 64 and may be a pulsed or continuous supply thereof. The presence of gas in the fragmentation region is detected using ionization gauge 65. After fragmentation, the Y-velocity of the ions, both ion of interest and ions

20   formed by fragmentation thereof is reversed by applying a voltage, static or dynamic to the end cap 62. This causes the ions to accelerate away from the end cap 62 and towards the aperture in the fragmentation device 60.

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The beam of fragmented ions will exit the fragmentation device 60 and may pass through a further ion optical arrangement 36 and will enter a field free region between electrodes 31 and 32. If electrode 31 is pulsed to voltage V once again, then the beam of fragmented ions will be accelerated substantially orthogonally of the Y direction through electrode 34 and into the measurement chamber 50.

When collision with a gas is used to fragment an ion of interest, the collision energy will be partitioned amongst the fragment ions formed. The fragment ions have a similar velocity to the ion of interest from which they are formed which means that the collision energy in the case of singly charged ions will be partitioned approximately as a fraction m_d/M_p of the energy of the ion of interest wherein m_d is the mass value for the fragment ion and M_p is the mass value of the ion of interest. This therefore means that the fragment ions will have different angles after entry back into the measurement chamber 50 and therefore there will be a different path of travel for each different fragment ion of different m/z ratio. In order to ensure that all of the fragment ions ultimately impinge upon the detector 70, it is necessary to minimise the difference in Y distance travelled. This can be achieved in a number of different ways. Firstly, if desired, a voltage can be applied to the fragmentation device 60, such that the fragment ions can receive an additional acceleration on exit. The lighter fragments are accelerated to a higher Y-velocity than the heavier fragments which assists

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in minimisation of the difference in path of travel in the Y-direction of the

fragment ions in the measurement chamber 50.

The energy and coordinates f ions of interest and of the fragment ions

may also be controlled using collisional damping, collisional focusing or

5   collisional reflection.

Alternatively, if gas collisions using other energies are necessary then

there are several possibilities which may be employed. Firstly, the energy

could be changed by scaling voltages on all electrodes of the whole mass

spectrometer so that the shape of trajectories does not change while

10   efficiency of CID is strongly varied. Secondly, it could be changed by

applying additional accelerating or decelerating voltage along the gap

between the extraction device 30 and the fragmenting means 60 prior to

the entrance of the precursor ions into this gap. While all beam section S

of the ions is already travelling inside the fragmenting means 60, this

15   voltage could also be changed in order to optimise forthcoming extraction

of fragments. Any type of ion optical arrangement 36 either transmitting

or reflecting, static or dynamic could be disposed between the extraction

device 30 and fragmentation device 60. For example, a controlled retarding

voltage could be used as a means for distinguishing fragment ions from

20   other charge state ions. Thirdly, energy of collisions could be varied inside

the fragmenting means 60 by an additional radio-frequency or impulsive

excitation of the ions using voltages applied across or along the focusing

means 66. In particular, cycles of excitation/de-excitation could be the most promising as after each cycle the precursor ions (as well as heavier fragments) return to the axis making their focusing easier. By suitable arrangement of the voltages on the various electrodes it can be arranged

5   such that the beam of fragmented ions travel through measurement chamber 50, are reflected by the ion mirror 40 and then impinge upon the detector 70 whereby measurement of a mass spectrum can be made from these fragmented ions. This situation is illustrated in Fig. 2. It can be seen therefore that using the apparatus shown in Fig. 1 and Fig. 2 of the

10   drawings that a tandem time-of-flight mass spectrometer can be provided without the necessity to utilise two separate mass spectrometer chambers linked together. Furthermore, the arrangement of the present invention is clearly versatile insofar as the mass spectrometer can operate either as a single mass spectrometer or as a tandem mass spectrometer simply by

15   arranging for the extracted ion beam to either be fragmented prior to detection or by arranging for the extracted beam simply to be detected without fragmentation. It will be appreciated that this gives rise to considerable savings as to cost and complexity of the apparatus.

An alternative embodiment of apparatus in accordance with the

20   present invention is shown in Fig. 4. In this embodiment, additional pairs of deflector plates 51 and 52 are provided in the measurement chamber. The pairs of deflector plates 51, 52 act to deflect an ion beam passing

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through the measurement chamber 50. The first pair of deflector plates 51

deflects the incoming ion beam so as to avoid the detector 70 after

reflection. The second pair of deflector plates 52 deflects the ion beam by

an equal amount in the opposite direction to plates 51. The nett effect of

5   plates 51 and 52 is the parallel displacement of the ion beam in a direction

illustrated as Z in Fig. 4 with minimum time-of-flight aberrations. The beam

enters the fragmentation device 60 which is vertically displaced relative to

the detector 70 and ion source 10. Of course, if the deflection plates 51

do not have voltage applied then the incoming ion beam will simply, after

10   reflection in the ion mirror 40, impinge upon the detector without

fragmentation having occurred.

It is of course to be understood that the invention is not intended to

be restricted to the details of the above embodiment which are described

by way of example only.

15   Thus, for example, it is possible to improve the duty cycle of the

spectrometer of the invention by arranging for the voltage pulse which

causes the ion beam to enter the measurement chamber 50 from the ion

source 10 to be coincident in time with the pulse to cause the fragment ions

to enter the measurement chamber 50 from the fragmentation device 60.

20   In the described embodiment (Figs. 1 and 2) there is an absence of any

obstacles in the direction Y between the ion optical arrangement 20 and

the fragmentation device 60 along extraction device 30. The extraction

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device may of course be constructed in several sections. In these circumstances, a further electrode 37 is provided between the ion source 10 and fragmentation device 60 which can be pulsed appropriately with a voltage to ensure that ions do not pass from ion source 10 to fragmentation

5   device 60 directly along extraction device 30. Also, for example, successive tandem experiments (usually referred to as $(MS)^n$) could be carried out in this instrument by having a second fragmentation module or other means of fragmentation between the ion source 10 and the extraction means 30, or located above or below the ion source. Alternatively, ion

10   optical arrangement 20 could be used to reflect the beam.

Furthermore, if desired, more than one detector 70 may be provided in the measurement chamber 50.

Furthermore, it is possible if desired for the initial acceleration into the chamber 50 and the deceleration on exit from the chamber 50 and

15   fragmentation to be carried out by suitable means disposed at any convenient position in the spectrometer, and hence it may be possible to omit the ion mirror from the measurement chamber 50.

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CLAIMS

1.   A mass spectrometer of the time-of-flight kind comprising an ion source to produce ions for analysis, said ions having a velocity in a first direction, means to impose a velocity in a second direction on said ions to

5   cause the ions to enter a measurement chamber in which is disposed a detector, means to reduce the velocity of ions of interest of a selected m/z ratio in said second direction to substantially zero whereby the velocity in a first direction causes only said ions of interest to enter a fragmentation means which acts to fragment the ions into smaller mass ions, means to

10   impose a further velocity in a second direction on said smaller mass ions to cause said smaller ions to move towards the detector for detection, said detector being operable to produce a mass spectrum in accordance with said detected smaller mass ions.

2.   A mass spectrometer according to claim 1 wherein said means to

15   reduce the velocity of ions of interest comprises a pair of parallel spaced apart electrodes, one of fixed voltage and the other of variable voltage (relative thereto) whereby an electric field can be created therebetween which acts to decelerate all ions passing into the field, the variable voltage being selected such that only ions of interest are decelerated to substantially

20   zero velocity and can enter the fragmentation means.

3.   A mass spectrometer according to claim 1 wherein said means to impose a velocity in said second direction comprises a pair of parallel

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spaced apart electrodes, one of fixed voltage and the other of variable voltage relative thereto whereby an electric field can be created therebetween which imposes a velocity in the second direction in the ions.

4.   A mass spectrometer according to claim 2 or claim 3 wherein one of said electrodes is perforated so as to allow ions to pass therethrough into the measurement chamber.

5.   A mass spectrometer according to any one of claims 1 to 4 wherein the ion source and the fragmentation means are axially aligned in said first direction and are outside said chamber.

6.   A mass spectrometer according to any one of claims 1 to 5 wherein said means to impose a velocity in said second direction to cause the ions to enter the measurement chamber and the means to reduce the velocity of ions of interest to substantially zero velocity are formed by a single pair of parallel spaced apart electrodes, one of fixed voltage and the other of variable voltage, each electrode being split into at least two separate electrode parts.

7.   A mass spectrometer according to any one of claims 1 to 6 wherein an ion reflector is provided in the measurement chamber which acts to selectively direct ions in the chamber towards the detector or to the fragmentation means for fragmentation prior to detection.

8.   A mass spectrometer according to any one of claims 1 to 7 wherein the fragmentation means causes fragmentation of the ions by one of,

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collision induced dissociation, surface induced dissocation or photo induced

dissociation.

9.   A mass spectrometer according to claim 8 wherein said fragmentation

means includes means to reverse the direction of travel of the ions of

5   interest and smaller mass ions after fragmentation to allow ejection from the

fragmentation means.

10.   A mass spectrometer according to claim 8 or claim 9 wherein said

fragmentation means also includes ion focussing means to focus ions on
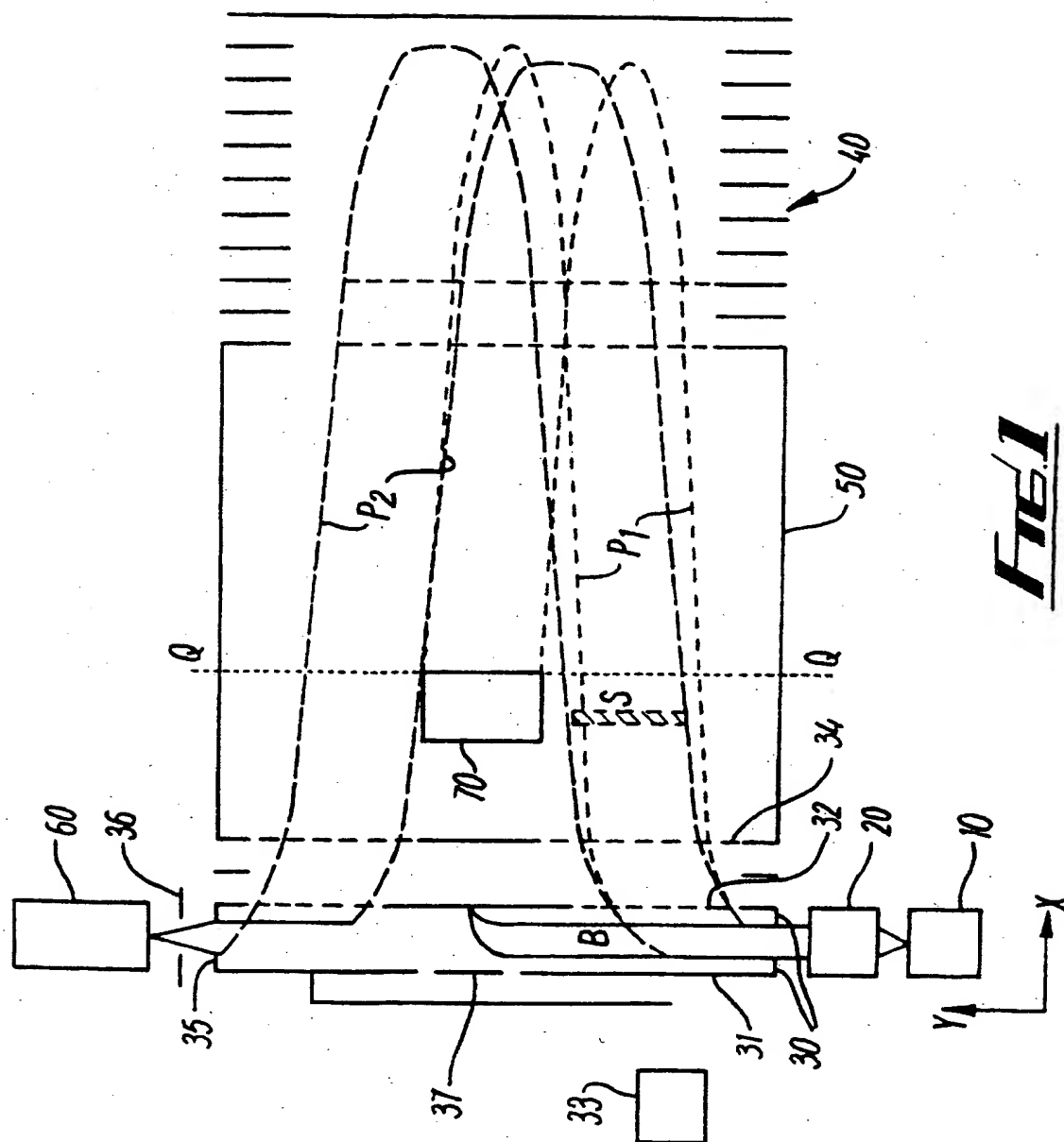
ejection from the fragmentation means.

10   11.   A mass spectrometer according to any one of claims 1 to 10 wherein

a pair of deflection means are provided in said measurement chamber, one

of which acts upon entry of ions into said chamber to direct said ions

around said detector towards said fragmentation means and a second of

said pair of deflection means acts to direct said fragmented ions towards

15   the detector for detection.

12.   A mass spectrometer according to claim 11 wherein each of said pair

of deflection means comprises a pair of parallel spaced apart plates

connected to a voltage supply.

13.   A mass spectrometer according to any one of claims 2 to 12 wherein,

20   in use, said means to impose a velocity in a second direction to cause said

ions to enter said measurement chamber is operable to impose said velocity

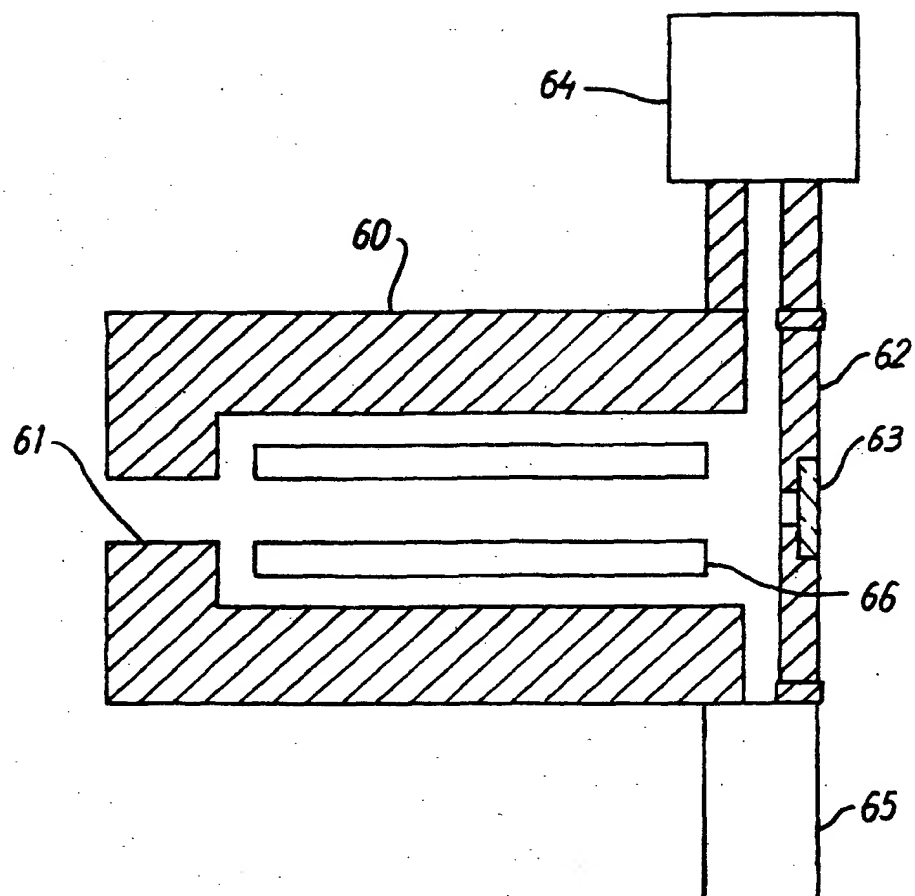simultaneously with ejection of fragmented ions from the fragmentation

means.

Fig 1

$P_{heavier}$

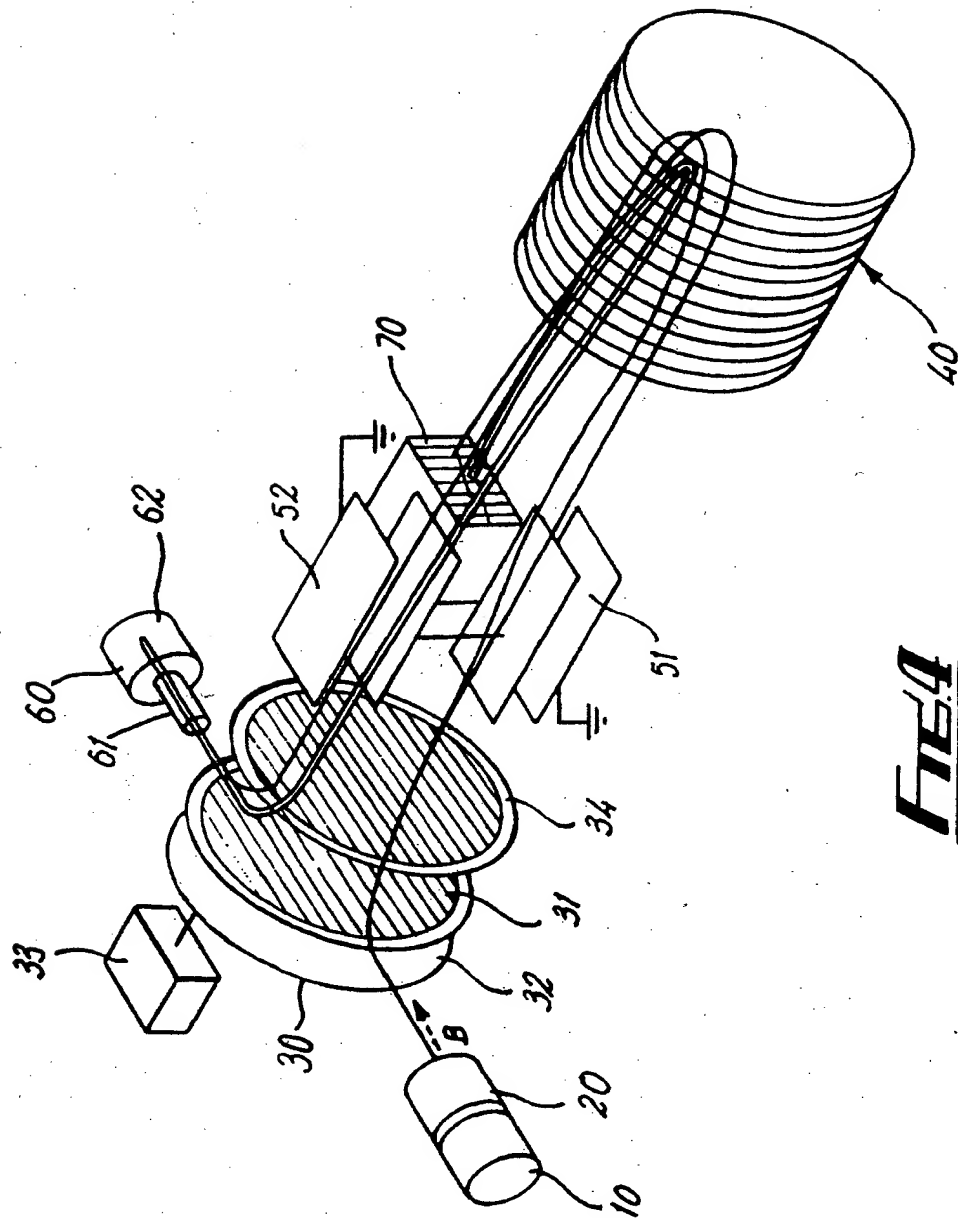$P_{lighter}$

FIG. 2

FIG. 3

FIG.4

Inte.   >nal Application No
PCT/GB 97/01552

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   H01J49/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 851 669 A (ABERTH WILLIAM) 25 July 1989	1,2,5,7, 8,11
A	see column 7, last paragraph; figure 4	6,12,13
A	US 5 202 563 A (COTTER ROBERT J ET AL) 13 April 1993 see column 7, line 56 – column 8, line 27; figure 1	1
A	GB 2 274 197 A (KRATOS ANALYTICAL LTD) 13 July 1994 see abstract	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 October 1997	10. 10. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hulne, S

INTERNATIONAL SEARCH REPORT

...ormation on patent family members

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GB 2274197 A	13-07-94	NONE	

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(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
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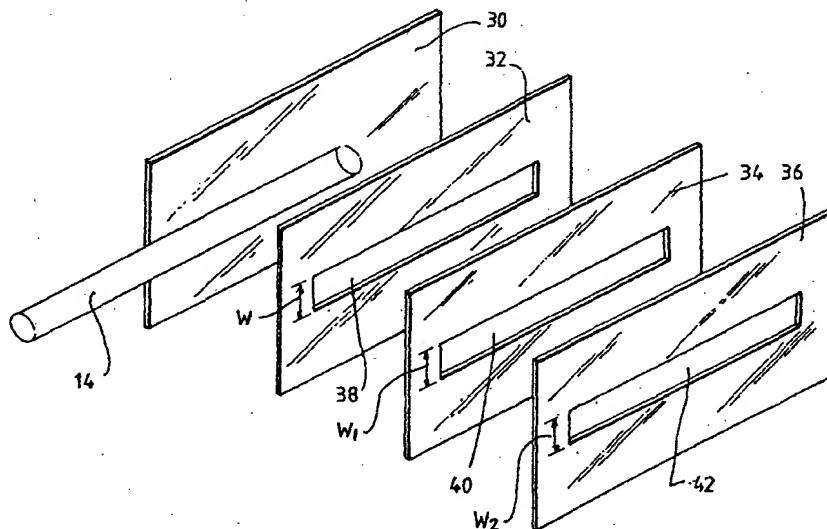
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(54) Title: A TIME OF FLIGHT MASS SPECTROMETER INCLUDING AN ORTHOGONAL ACCELERATOR

(57) Abstract: A time of flight mass spectometer is disclosed which includes an ion source (10), an orthogonal accelerator (20), a reflectron (24) and a detector (22). The orthogonal accelerator (20) has a first electrode (32) which is a gridless electrode and includes a slot which is elongated in the direction of an ion beam supplied to the orthogonal accelerator from the source (10). The orthogonal accelerator (20) has a second thin plate electrode having a slot parallel to the slot in the first electrode and a third electrode with a slot parallel to the slot in the first electrode. The electrodes produce a retarding field during an ion accumulation mode, and an extraction field during an ion extraction mode.

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A TIME OF FLIGHT MASS SPECTROMETER INCLUDING AN ORTHOGONAL ACCELERATOR

This invention relates to a time of flight mass
5   spectrometer including an orthogonal accelerator.

Time of flight mass spectrometers generally include an ion
source for producing a continuous or pulsed beam of ions
which are directed in a first direction.   The ions
10 generally pass through various electric focusing optics so
as to collimate the beam and to direct the beam to an
orthogonal accelerator.   The orthogonal accelerator pushes
ions in the ion beam out of the beam in a direction
transverse to the first direction into a flight tube so
15 that the ions travel along the tube and eventually arrive
at a detector.   The time taken to travel along the tube and
arrive at the detector is dependant on the mass of the ions
and therefore the detection of ions at different time
intervals can provide an indication of the mass of the ions
20 in the ion beam and therefore the material in the sample
substance which is being analysed and from which the ion
beam is formed.

Conventional orthogonal accelerators generally comprise a
25 number of electrodes at least some of which are in the
nature of grids.   Electric potentials are applied to the
various electrodes so as to force the ions to travel in the
direction transverse to the first direction.   The grid
electrodes enables some of the ions to pass through the
30 grid and therefore into the tube for detection at the
detector.

The grids in conventional orthogonal accelerators produce a
number of disadvantages including the fact that the grids
35 become covered by deposits and may start charging up thus
reducing mass peak stability, grids reduce sensitivity by
absorbing part of the beam and scattering transmitted ions,

and grids are difficult to mount reproducably.

The present inventor has found that the main problem which
grids cause is associated with the grid closest to the ion
5   beam which enters the orthogonal accelerator. Ions have
the lowest energy during accumulation in the acceleration
stage and therefore even small voltages induced by charge
contamination is enough to ruin the integrity of the beam
entering the orthogonal accelerator. This charge
10   contamination can result in an angular divergence of ions
out of the beam as the beam enters into the orthogonal
accelerator. The angular divergence induced by
contamination results in greatly increased time of flight
and geometrical aberrations which reduces a resolution of
15   the spectrometer. The influence of deposits on further
grids is orders of magnitude lower as those grids are
shielded by the first grid and also ions possess much
higher energies when they finally pass through those grids
during the extraction process from the orthogonal
20   accelerator.

The present invention may be said to reside in a time of
flight mass spectrometer including:
           means for producing a beam of ions and for
25   directing the beam of ions in a first direction;
           an orthogonal accelerator for receiving the beam
of ions and for accelerating ions in the beam in a
direction transverse to the first direction into a time of
flight cavity;
30   a detector for detecting the ions after travel
from the orthogonal accelerator through the time of flight
cavity; and
           wherein said orthogonal accelerator has;
           a plurality of electrodes for receiving electric
35   potentials, and for extracting ions in a direction
transverse to the first direction, one of the electrodes
being the first electrode through which ions are

transported during extraction of the ions in the transvers
direction by the orthogonal accel rator; and

        wherein the first electrode is a gridl ss
electrode including a slot which is elongated in the said
5   first direction.

According to the present invention the orthogonal
accelerator can operate in two modes. The first of the two
modes being an accumulation mode, in which inevitable stray
10   and scattered ions are prevented from bleeding into the
time of flight cavity by the field between the first
electrode and another of the pluralities of electrodes
while the beam stays far enough from the first electrode
not to be perturbed by the electric field created by the
15   first electrode; and the second mode being an extraction
mode when fields on both sides of the first electrode
change in such a way that the difference in field gradients
is not high enough to introduce noticeable time of flight
aberrations and angular scattering.
20
Preferably the width of the slot in the first electrode
does not exceed the largest distance from the slot to any
ion within the ion beam during the accumulation mode when
ions are accumulated in the orthogonal accelerator prior to
25   extraction in the transverse direction.

Preferably said first electrode forms together with further
electrodes of the plurality of electrodes, a retarding
field during the ion accumulation mode, and an extraction
30   field during the ion extraction mode in such a way that
minimum size of an ion packet of a given mass to charge
ratio both in space and time of flight is achieved at the
detector.

35   Preferably the orthogonal accelerator comprises;
            a flat back plate electrode;
            a thin plate electrode which forms said first

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electrode, the flat back plate electrode and the thin plate
electrode defining a space for receiving the ion beam which
is directed in the first direction;

a thin-plate second electrode having a slot
5   parallel to the slot in the first electrode;

a third electrode with a slot parallel to the
slot in the first electrode; and

wherein electric potentials on all electrodes are
variable independently, so that during the accumulation is
10   mode the voltage between the first and second electrodes is
retarding for ions and during the extraction mode all
voltages are changed in such a way that an extraction field
is formed for accelerating the ions in the transverse
direction.

15   Preferably the widths of the slots in the first and second
electrodes are equal, and the gap between the back plate
electrode and the first electrode is equal to the gap
between the second and third electrodes, and the gap
between the first and second electrodes being three times
20   smaller than the gap between the thin plate second and
third electrodes and two times bigger than the width of the
slots in the first and second electrodes.

Preferably the time of flight spectrometer includes ion
25   gating means, a reflectron and a lens, and wherein;
voltages applied during the extraction mode are
chosen in such a way that non uniform electric fields
provides both spacial and first or second order time of
flight focusing exactly in the plane of the ion gating
30   means;   the lens is elongated along the first direction
and has voltages applied to it in such a way that minimum
spacial size of ion packets is achieved at the detector;
and   voltages on the reflectron are adjusted in such a
35   way that minimum time of flights spread of ion packets is

achieved at the detector.

Preferably the ion beam in the first direction is directed
into the space between the back plate electrode and the
5   first electrode a minimum distance from the back plate
electrode.

Preferred embodiments of the invention of the invention
will be described, by way of example, with reference to the
10   accompanying drawings in which:
        Figure 1 is a schematic diagram of a time of
flight mass spectrometer;
        Figure 2 is a schematic diagram showing the
orthogonal accelerator according to the preferred
15   embodiment of the invention;
        Figures 3 and 4 are graph showing the application
of electric potentials during the accumulation mode and
extraction mode respectively for the embodiments shown in
Figure 2;
20   Figure 5 is a view of a second embodiment of the
invention;
        Figure 6 and Figure 7 are graphs showing a graph
of electric potential during an accumulation mode and
extraction mode applicable to the embodiment shown in
25   Figure 5; and
        Figure 8 is a schematic perspective view of the
orthogonal accelerator.

With reference to Figure 1, time of flight mass
30   spectrometers are well known and therefore the schematic
representation shown in Figure 1 is merely to provide a
basic outline of the position of the orthogonal accelerator
in the time of flight spectrometer. The spectrometer
generally comprises an ion source 10 which may be an
35   inductively coupled plasma ion source, an electro spray or
the like. Generally focusing optics and beam creating
optics 12 are provided for focusing and directing an ion

beam 14 from the source 10 in a first direction x. An
orthogonal accelerator 20 is provided for accelerating the
ion packets from the beam in a second direction y
transverse to the direction x into a time of pulse tube or
5   cavity. The ion packets accelerated from the orthogonal
accelerator 20 may be received directly by a detector 22
or, as in the case of Figure 1, a reflection 24 may be
provided for turning the ion packets 16 before they arrives
at the detector 22. An ion gate 17 is disposed in the path
10   of the ions for selectively filtering unwanted ions and a
lens 18 is provided for focusing of the ions 16.

With reference to Figures 2 and 8 the orthogonal
accelerator 20 most preferably comprises a flat back
15   electrode 30 which is held at a static potential U0. A
first electrode 32 forms a compensation electrode which is
approximately 0.2 mm thick and which is spaced from the
back electrode 30 by a distance of about 6 mm. A potential
U1 is applied to the electrode 32. A second electrode 34
20   forms a pull out and electrode is spaced from the electrode
32 by a distance of about 4 mm and is about 0.2 mm thick.
A potential U2 which is greater than the potential U1 (for
positive ions) is applied to the electrode 34. A further
30 mm downstream from the electrode 34 is a third electrode
25   36 which forms an exit electrode U3 which is about 1 mm
thick and is kept at the potential of the time of flight
cavity or tube 23 (see Figure 1). The electrodes 32, 34
and 36 are gridless solid plate electrodes which have a
slot 38, 40 and 42 respectively which is elongated in the
30   direction of the beam 14 (i.e. direction x) from the ion
source 10. The slot 38 has a width w (see Figure 8) of
about 4 mm, and the slot 40 has a width of W_1 of about
3 mm.

35   The exit electrode 36 is also preferably gridl ss and has
slot 42 which is also elongated in the direction of the ion
beam 14. The width W_2 of the slot 42 is about 3 mm.

Typically, (U2-U1) is > (U0-U3)/100, so that virtually no
fieled is experienced by ions moving n ar the back
electrode 30, while ions penetrating through the slot 38 of
the compensation electrode 32 experience a retarding field.
This field stops ions bleeding into the time of flight tube
or cavity 23 thus drastically reducing ion background.

During the extraction mode, a positive pulse P1 is applied
to the back electrode 30 and a negative pulse of amplitude
P2 is applied to the pull out electrode 34 less than 20 ns
later. Amplitudes of the pules are related as P2=P1x(1.2-
1.4) depending on beam divergence and position of the time
of flight focus. Also, P2=(U0-U3)x0.2.

The electrode 32 provides as low as possible electric
fields in the region of ion beam 14 during accumulation,
absorbs some scattered ions and also serves as a filed-
sustaining and focusing electrode during ion extraction.

A second embodiment is shown in Figures 5 to 7 in which the
only difference to that described with reference to Figure
2 is a grid as attached to the pull out electrode 34 and
thus the arrangement shown in Figure 5 may be regarded as
inferior to that shown in Figure 2. However, the
arrangement shown in Figure 5 allows the use of lower
static voltages (U2-U1)>(U0-U3)/300 and allows easier
tuning. In all modes and constructions, potential U1 is
variable; | U1-U0 |>0.001x(U0-U3). The acceleration stage
of the orthogonal accelerator in both Figures 1 and Figure
2 may also be combined with ion gating (eg. flat deflection
plates activated by short electric pulses) at the plane of
the time of flight focusing. In this case, potentials P1,
P2 and U1 could be tuned to provide simultaneous second-
order focusing on the time of flight as well as spacial
focusing. The later allows to improve mass resolution of
the ion gating means.

The deflection of the ion beam during the accumulation mode is minimised by choosing the width of the slot in the compensation electrode 32 small compared to the distance from the slot 2 ions in the beam 14. However, this slot 38

5 should be big enough to allow all ions of the beam to pass through during the subsequent extraction mode. It has been found experimentally that in such a construction contamination from the ion beam is absorbed mainly by electrodes downstream of the compensation electrode 32 and

10 therefore influences of contamination on the ion beam is greatly reduced.

Preferably all of the electrodes 30, 32, 34 and 36 are formed from non-magnetic stainless steel.

15 In other embodiments the speedometer may include ion trapping or collisional cooling or additional focusing/deflecting ion optics before the orthogonal accelerator.

20 The slots in the electrodes 32, 34 and 36 could be formed by electroetching, electroforming or laser cutting

In some embodiments of the invention a slotted plated electrode is located between the first electrode 32 and the back electrode 30 to assist in confining the electric

25 fields produced by the electrodes 32, 34 and 36. This plate electrode does not play any part in the ion beam formation and is usually at the potential of the back plate

30 electrode 30 or another electrode to which it is connected.

In other embodiments first interfaces may be utilised between the ion source and the orthogonal accelerator 20 including collisional cooling or chemical reactions in RF

35 multipoles at elevated pressures, MS-MS stages and additional ionoptics. More than one reflectron or additional lenses may also be utilised within the time of

flight cavity 23. Furthermore, the orthogonal accelerator 20 could omit the electrode 36 (and therefore be a two-stage orthogonal accelerator, or electrode 32 may be pulsed (e.g. instead of the electrode 34).

5

Ion sources include the ICP electrode as described, or ES, APCI, EI-CI-MALDI sources.

Since modification within the spirit and scope of the

10 intention may readily be effected by persons skilled within the art, it is to be understood that this invention is not limited to the particular embodiments described by way of example hereinabove.

15

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.   A time of flight mass spectrometer including:

        means for producing a beam of ions and for
directing the beam of ions in a first direction;

        an orthogonal accelerator for receiving the beam
of ions and for accelerating ions in the beam in a
direction transverse to the first direction into a time of
flight cavity;

        a detector for detecting the ions after travel
from the orthogonal accelerator through the time of flight
cavity; and

        wherein said orthogonal accelerator has;

        a plurality of electrodes for receiving electric
potentials, and for extracting ions in a direction
transverse to the first direction, one of the electrodes
being the first electrode through which ions are
transported during extraction of the ions in the transverse
direction by the orthogonal accelerator; and

        wherein the first electrode is a gridless
electrode including a slot which is elongated in the said
first direction.

2.   The spectrometer of claim 1 wherein the width of
the slot in the first electrode does not exceed the largest
distance from the slot to any ion within the ion beam
during the accumulation mode when ions are accumulated in
the orthogonal accelerator prior to extraction in the
transverse direction.

3.   The spectrometer of claim 1 wherein said first
electrode forms together with further electrodes of the
plurality of electrodes, a retarding field during the ion
accumulation mode, and an extraction field during the ion
xtraction mode in such a way that minimum size of an ion
packet of a given mass to charge ratio both in space and
time of flight is achieved at the detector.

4.   The spectrometer of claim 1 wherein the
orthogonal accelerator comprises;

        a flat back plate electrode;

        a thin plate electrode which forms said first

5   electrode, the flat back plate electrode and the thin plate
electrode defining a space for receiving the ion beam which
is directed in the first direction;

        a thin-plate second electrode having a slot
parallel to the slot in the first electrode;

10   a third electrode with a slot parallel to the
slot in the first electrode; and

        wherein electric potentials on all electrodes are
variable independently, so that during the accumulation
mode the voltage between the first and second electrodes is

15   retarding for ions and during the extraction mode all
voltages are changed in such a way that an extraction field
is formed for accelerating the ions in the transverse
direction.

20   5.   The spectrometer of claim 1 wherein the widths of
the slots in the first and second electrodes are equal, and
the gap between the back plate electrode and the first
electrode is equal to the gap between the second and third
electrodes, and the gap between the first and second

25   electrodes being three times smaller than the gap between
the thin plate second and third electrodes and two times
bigger than the width of the slots in the first and second
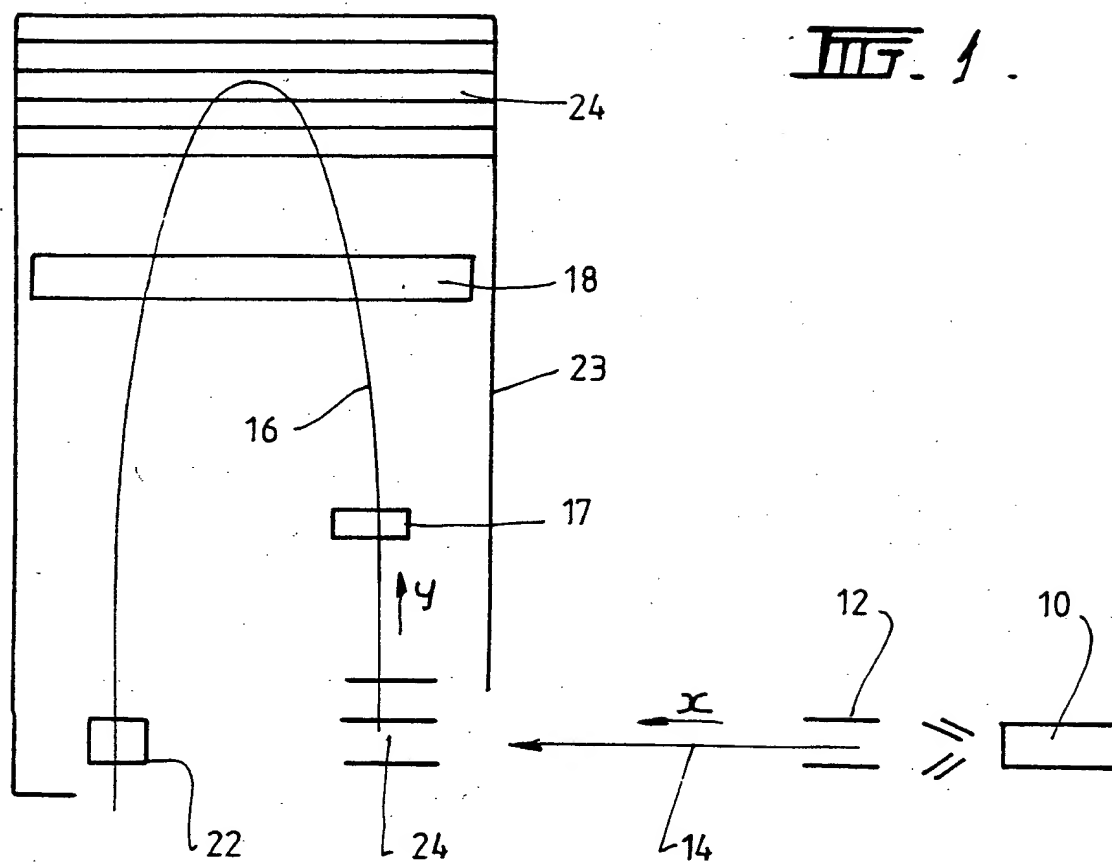electrodes.

30   6.   The spectrometer of claim 1 wherein the time of
flight spectrometer includes ion gating means, a reflectron
and a lens, and wherein;

        voltages applied during the extraction mode ar
chosen in such a way that non uniform electric fields

35   provid s both spacial and first or second order time of
flight focusing exactly in the plane of the ion gating
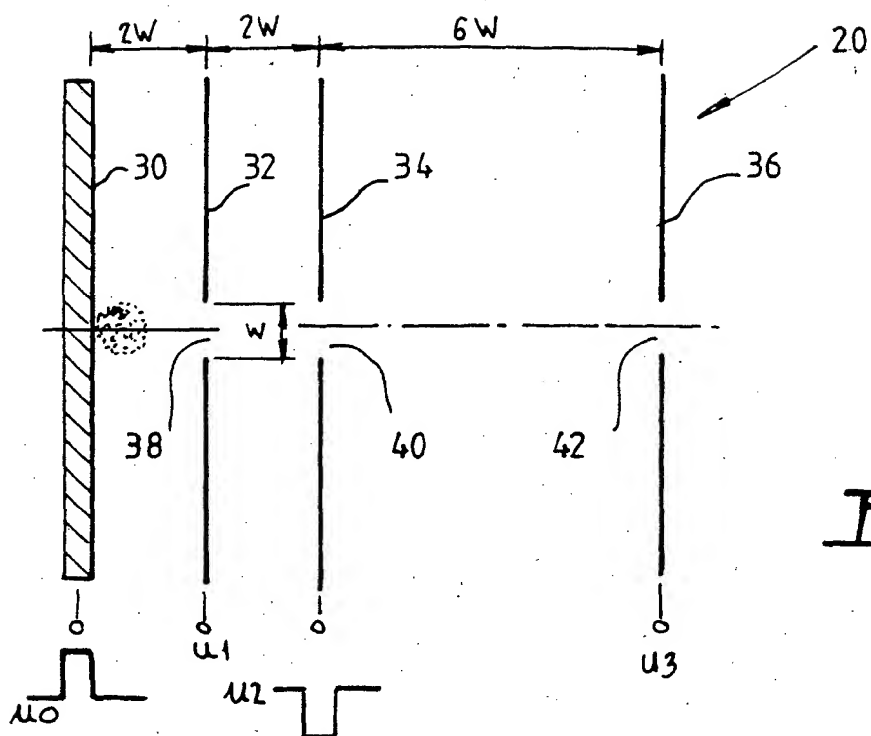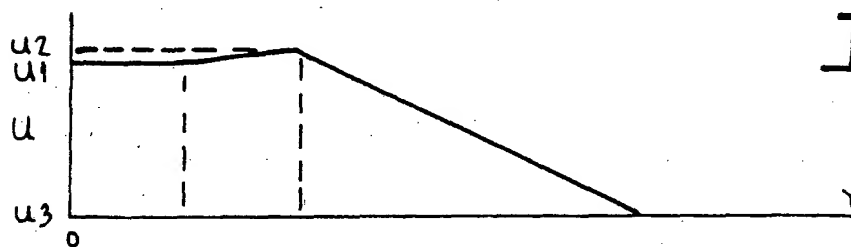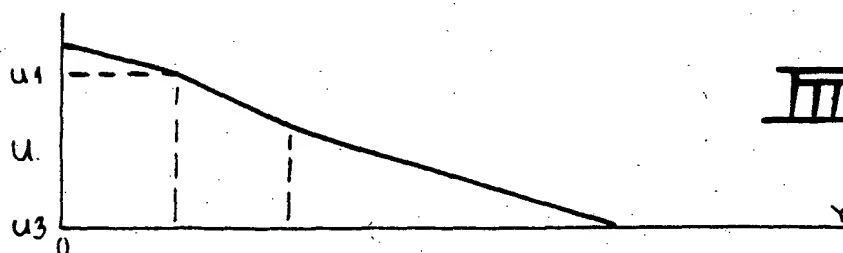means;

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the lens is elongated along the first direction
and has voltages applied to it in such a way that minimum
spacial size of ion packets is achieved at the detector;
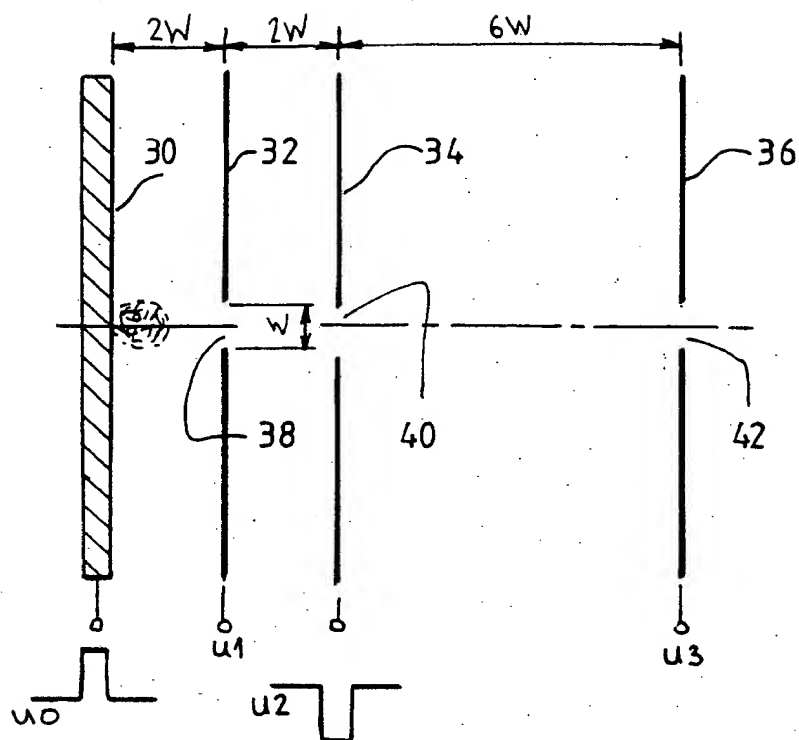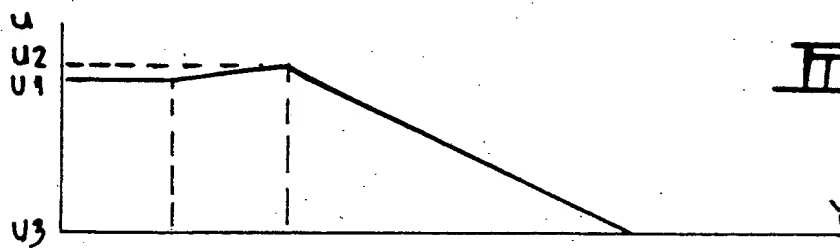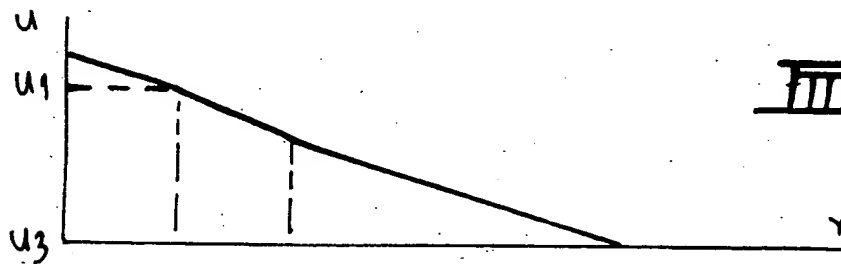and

5   voltages on the reflectron are adjusted in such a
way that minimum time of flights spread of ion packets is
achieved at the detector.

7.   The spectrometer of claim 1 wherein the ion beam
10   in the first direction is directed into the space between
the back plate electrode and the first electrode a minimum
distance from the back plate electrode.

FIG. 1.

FIG. 2.
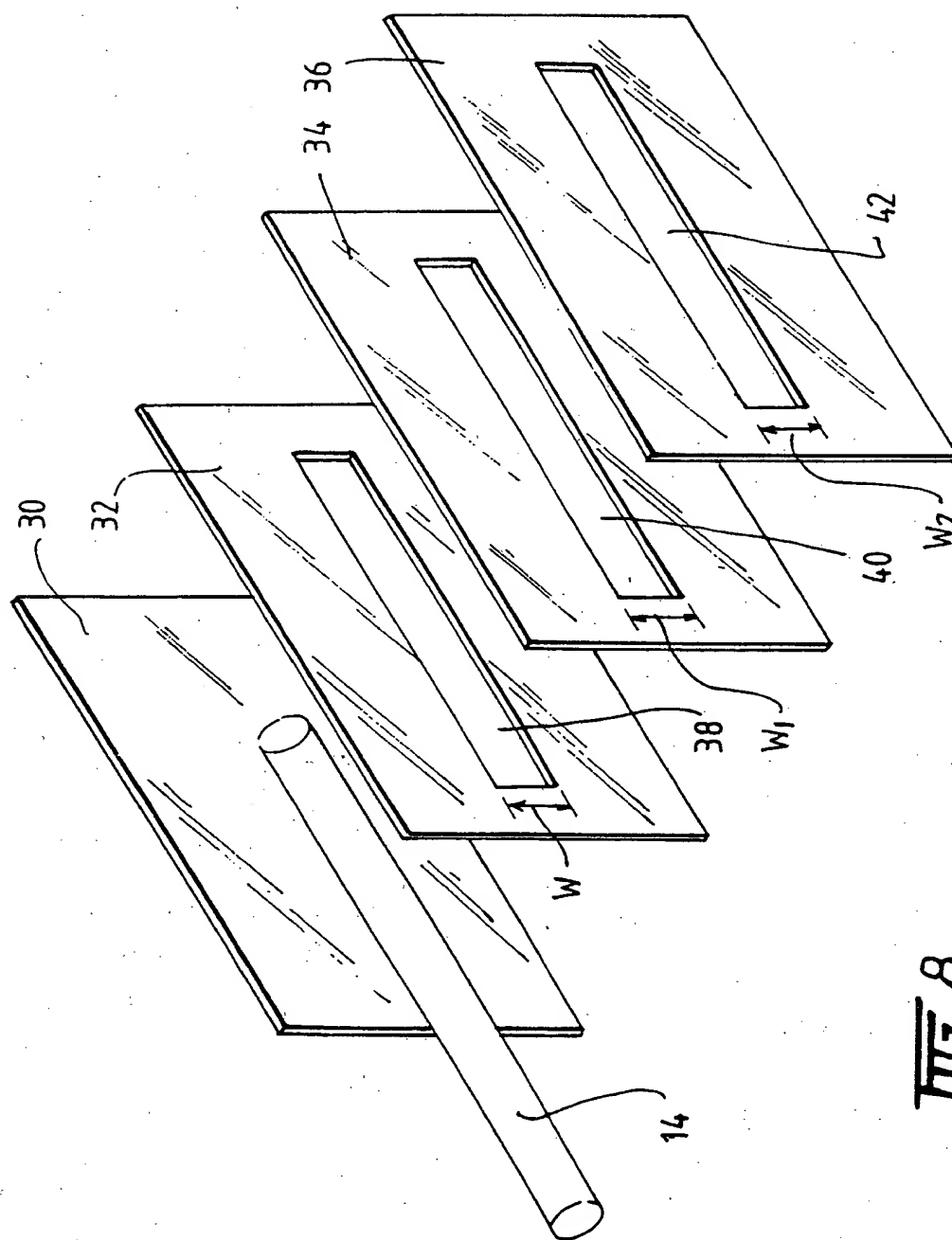

FIG. 3.

FIG. 4.

FIG. 5.

FIG. 6.

FIG. 7.

FIG. 8.

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]:   H01J 49/40

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT and JAPIO with key-words: 'time of flight', TOF, gridless, slot, electrode, orthogonal, accelerator

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 97/48120 A (HD TECHNOLOGIES LIMITED) 18 December 1997 page 4 line 18 to page 5 line 3, page 6 line 14 to page 7 line 19, figure 1 page 7 lines 10 to 18, figure 1	1 - 3, 7 4 - 6
Y	US 5 464 985 A (CORNISH & COTTER) 7 November 1995 columns 5 and 8 to 11	4 - 6

☐ Further documents are listed in the continuation of Box C	X	See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 6 November 2000	Date of mailing of the international search report 1 0 NOV 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorised officer **Ross Burdon** Telephone No : (02) 6283

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	97/48120	AU	30411/97	GB	9612091
US	5 464 985		- none -		

END OF ANNEX